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Chalcopyrite compound semiconductors for thin film solar cells

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Chalcopyrite semiconductors are used in thin film solar cells with the highest efficiencies, in particular for flexible solar cells. Recent progress has been made possible by an alkali post-deposition treatment. Other important trends are the development of tandem cells and of ultrathin solar cells. Recent progress has forwarded the understanding of off-stoichiometry and of bulk defects in these materials.

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Introduction

$Cu(In,Ga)Se_2$ is an alloy of $CuInSe_2$ and $CuGaSe_2$ which both crystallize in the chalcopyrite structure. It is a direct band gap semiconductor, used as absorber in thin film solar cells, which present a new generation of photovoltaic technologies. The advantages of thin film solar cells are low cost based on their low material and energy consumption, short energy pay back times, flexibility in design and light weight (see e.g. the White Paper on http://cigs-pv.net). Laboratory size solar cells have reached 22.6% of certified power conversion efficiency [1]. Commercial modules reach 16% efficiency (see Ref. [2] and the websites of various producers).

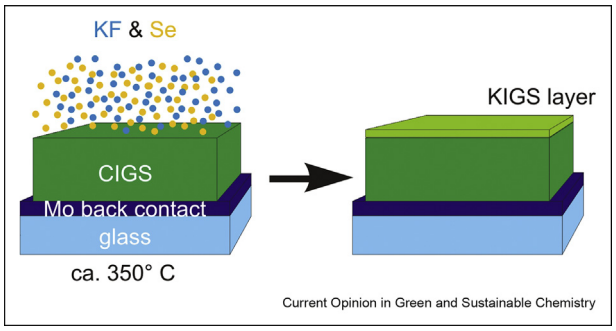
In the last three years there has been tremendous progress in efficiency based on an alkali post-deposition treatment. Even higher efficiencies are aimed at by the use of tandem solar cells based on thin film cells. Further progress has been made in the optical and the back contact design of ultrathin solar cells which use even less raw materials. The understanding of the role of off-stoichiometry and of defects has been expanded. These topics are discussed in detail in the following.

Alkali treatment

The last three years have seen a dramatic increase in the efficiency of $Cu(In,Ga)Se_2$ solar cells, based on a newly developed alkali treatment [3]. The role of sodium had long been recognised [4–6] and it had been thought that potassium has similar effects [7,8]. The potassium postdeposition treatment has led to a world record efficiency of 20.4% at that time [3], which is still the record efficiency of any flexible solar cell. The treatment is performed by depositing a small amount of alkali fluoride in the presence of Se pressure onto the surface of the film during cool down after growth [3], see Figure 1. Originally, the postdeposition treatment had been developed to introduce Na into $Cu(In,Ga)Se_2$ films grown at comparatively low temperatures. It was shown for these low temperature processes to be more beneficial than providing Na by a precursor [9]. The impeded annihilation of stacking faults in the presence of Na contributes to this observation [10]. Meanwhile the postdeposition treatment with K or heavier alkalis has been shown to be efficient for a low and high temperature processes and has led to a series of new record efficiencies [11–13]. Finally, it was found that treatment based on other heavier alkalis improves the efficiency even further, leading to the current world record efficiency of 22.6% [1]. An efficiency of 22.8% has been reported, but not certified, yet [13]. Alkali treatment also improves the efficiency in a full size industrial production process [14]. For absorbers prepared by a co-evaporation process, the treatment is done in-situ at the end of the process [1,3,14,15]. Ex-situ processes, where the alkali treatment is performed outside the deposition chamber were also shown to improve the efficiency [13,16–18]. It was found that the treatment is effective for sulphur containing absorbers based on $Cu(In,Ga)(S,Se)_2$ [13]. All these investigations found the improvement due to an increase in open-circuit voltage. A large amount of research activity has been directed into understanding the effects of the alkali treatment. The main observations are: (i) the alkali treatment creates a layer of different composition at the surface and (ii) leads to an ion exchange within the whole absorber layer, which influences the electronic properties.

(i) The potassium treatment creates a completely Cu-depleted surface layer, which can be continuous [3,16] or structured [15], depending on the exact treatment conditions. The Cu-depleted layer was found to have a wider surface band gap than

Figure 1



Schematics of the alkali postdeposition treatment.

untreated absorbers [16,19] and to consist of K-In-Ga-Se compounds [15,20], although Ga is also reduced at the surface [3]. The layer is sometimes referred to as the KIGS layer. One effect of this surface layer is that it allows for a thinner buffer layer and thus more photons reaching the absorber layer [3,12,14]. A second effect of the surface layer is to reduce surface recombination [17,21]. Both effects are associated with the Cu-depletion at the surface and to increased Cd indiffusion [3,21,22]. Furthermore it was observed that with alkali treatment it is possible to increase the efficiency of solar cells with higher Ga content and thus higher band gap [12]. Attempts to grow the KIGS layer directly have also led to improved short circuit currents [23].

(ii) An ion exchange takes place throughout the absorber, where the heavier alkalis replace the lighter ones [1,3,20]. This ion exchange is also observed when the lighter alkalis are supplied by the substrate glass [1]. Alkalis are well known to accumulate at the grain boundaries (see e.g. Refs. [24–26]). Whether the ion exchange reaction is limited to the grain boundaries or appears also in the bulk is not known currently. An influence of the alkali treatment on the doping level has been observed, however a reduced [21] or an increased doping level [27] was found in each case compared to absorbers containing Na, but without potassium treatment. It was recognised that alkali treatment leads to an increased carrier lifetime [27,28], which goes along with an increased photoluminescence intensity [27,29], indicating reduced non-radiative recombination as the basis for the improved open-circuit voltage [27]. Temperature dependent photoluminescence measurements hint at a reduced amount of potential fluctuations in K treated samples [28].

Tandem cells

A more radical approach to improving the efficiency is the use of tandem cells. In the past considerable effort has been extended to developing tandem solar cells based on wide gap and low gap $Cu(In,Ga)Se_2$ [30–34] or related compounds [35]. This effort has been hampered so far by the limited efficiency obtained with $CuGaSe_2$ solar cells: best efficiency so far has been 11.2% [36]. With the recent development of perovskite solar cells (see the review in this issue) tandems are now made with these cells as top cells [37–40]. An efficiency of 20.5% has been reached with a 4-terminal cell [40] and of 17.8% with a 2-terminal monolithically integrated minimodule (see press release at e.g. https://www.kit.edu/kit/english/pi_2016_133_record-for-perovskite-cigs-tandem-solar-module.php). These record efficiencies of the tandem devices are better than the efficiencies of the top or bottom device constituting the tandem cells.

The sulfide semiconductor $Cu(In,Ga)S_2$ covers the ideal band gaps for a top cell in a tandem application with $CuIn(Ga)Se_2$ or Si [41,42]. The field has been recently renewed by the development of a cell with efficiency above 15% based on higher substrate temperatures [43]. Open-circuit voltages above 970 mV have been achieved [44].

Ultrathin cells

Another current trend in $Cu(In,Ga)Se_2$ solar cells is to make the absorber thinner to save costly In. When the absorber thickness becomes lower than 0.5 μm the short circuit current decreases considerably [45,46]. Therefore optical confinement is needed. This is achieved by optimising reflexion and absorption properties [46,47], by structures optimised for back side illumination [48,49] or by light trapping [50]. Light trapping can be achieved by using plasmonic structures: various approaches have been applied: Ag nanostructures at the back contact [51], at the surface of the cell [52], or at the surface of the absorber [53]. Generally a loss in open-circuit voltage is observed. Only one approach with plasmonic structures, has so far led to an actually improved efficiency compared to similar cells without nanostructures: SiO_2 nanoparticles at the back contact [54].

An additional challenge is posed by back surface recombination, which decreases current and voltage is ultrathin solar cells [55]. The recombination activity of the back surface seems to depend on the details of the preparation process and the cell structure: it has been observed to have only minimal influence in certain cases [56,57], whereas in others a serious reduction of the open-circuit voltage has been observed for absorbers thinner than 500 nm [45,58]. In any case an improved current collection is observed with passivated back contacts. Two approaches have been successful, based on insulating or conductive oxide layers. A non-conductive Al_2O_3 or SiO_2 passivation layer with point contact openings has been successful [58–62]. The

openings are achieved in a stochastic arrangement by CdS nanoparticles, which are etched after the oxide deposition [58–60], or in an ordered arrangement by electron beam lithography [61] or by plasma etching through a mask [62]. A structured layer has additional positive light trapping effects [62]. A conductive SnO_2:F layer has also been demonstrated as a passivated back contact [63].

The best efficiencies obtained with ultrathin cells up to now are: 13.5% with a 385 nm thick absorber [60], 11.8% with a 240 nm thick absorber [61] and 9% with a 190 nm thick absorber [62].

Cu-rich chalcopyrite

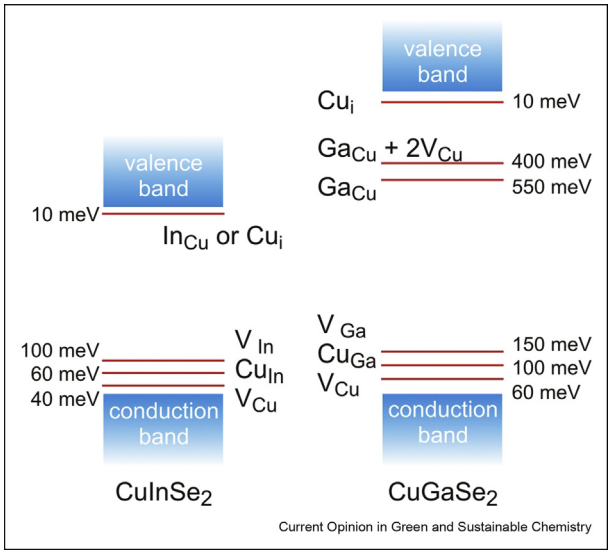
All aforementioned Cu(In,Ga)Se_2 solar cells are based on Cu-poor material, i.e. material with a sub-stoichiometric Cu content. Solar cells based on Cu-poor material always show better efficiencies [64–66], although Cu-rich material shows the better semiconductor properties with lower defect concentrations and better transport properties [67]. It has also been shown that the phase transition between Cu-poor and Cu-rich material is essential for the stress release in the films during growth [68]. It has been long understood that the lower efficiency of Cu-rich solar cells is due to recombination at or near the interface, which limits the open-circuit voltage [64]. This recombination can be suppressed by an In-Se surface treatment [65] or by a potassium treatment [17]. In pure $CuInSe_2$ solar cells (without Ga) the surface treatment leads to efficiencies of Cu-rich solar cells equal to Cu-poor ones [69], whereas in Ga-containing absorbers the surface treatment leads to an improvement of the open-circuit voltage, but not to a complete recovery of the values obtained in Cu-poor absorbers [66]. It was only recently understood that this difference is not in the first place due to a difference in interface properties, but to bulk properties of Cu(In,Ga)Se_2: in pure $CuInSe_2$ the quasi-Fermi level splitting, which is a measure of the open-circuit voltage an absorber could achieve, is higher in Cu-rich material than in Cu-poor [70,71], whereas in Cu(In,Ga)Se_2 (with Ga) the quasi-Fermi level splitting is lower in Cu-rich material than in Cu-poor, already in the absorber without any interface [72]. It has been proposed that the difference is due to a deep Ga_{Cu} antisite defect [73,74], which forms a less detrimental pair with copper vacancies in Cu-poor material.

Bulk defects

This observation shows once more that, although the interface is essential in the functioning of the solar cell, the bulk defects play an important role in the recombination behaviour. Furthermore they influence the electronic structure of the interface. A review of earlier work on grain boundaries and point defects and their role for doping and metastable effects can be found in Ref. [75].

Recently, progress has been made in determining the atomic structure of point defects: positron annihilation, which is sensitive to vacancy type defects, found the dominating vacancy defect in $CuGaSe_2$ to be the Cu-Se double vacancy, whereas in $CuInSe_2$ the double vacancy dominates only in Cu-poor material, whereas Cu-rich material contains single Cu-vacancies as the dominating vacancy type [76]. Cation related point defects have been detected by neutron diffraction in $CuInSe_2$ [77] and $CuGaSe_2$ [78]: in both cases Cu vacancies are found in Cu-poor material, in $CuInSe_2$ additional In_{Cu} antisites account for the Cu deficiency, whereas in $CuGaSe_2$ Ga interstitial were found. In Cu-rich $CuInSe_2$ the only defect detected is the Cu_{In} antisite, which is also present in Cu-poor material. It should be kept in mind that neutron scattering has a high detection limit for defects in the % range [79]. In fact, high defect densities have been observed in $CuInSe_2$ [77], above 10^{20} cm^{-3}. Since experimental doping densities are in the range of 10^{15}–10^{17} cm^{-3} (see e.g. Refs. [21,27,80,81]), defects must compensate and neutralise each other. Possible is also neutralisation with other defect types that have not been observed in the neutron scattering study, like anion related defects. In Cu-poor Cu(In,Ga)Se_2 thin films the presence of Na is essential to reach sufficient doping levels [6,80,82]. Neutron diffraction studies show that the addition of Na leads to a decrease of In_{Cu} antisite donors [83], which can explain the increase in p-type doping with the addition of Na. It has been theoretically predicted that while Na is likely to take interstitial sites, K is more likely to go on substitutional sites [84]. In addition to progress in the experimental characterisation of point defects, their theoretical description has evolved as well with the use of hybrid functionals in DFT

Figure 2



A proposal for defect structures and approximate defect energies based on the experimental and theoretical studies discussed in the text.

calculations. A number of recent papers use hybrid functionals to calculate defect energies in the gap and their formation energies [85–88]. It is generally agreed that three more or less shallow acceptors exist, in agreement with photoluminescence studies [75,89–91]: the Cu vacancy V_{Cu}, the Cu_{In} antisite, and the In or Ga vacancy V_{In} or V_{Ga}. Most calculations find that the In or Ga vacancy has a rather high formation energy [85,86,88] and it is thought to be unlikely the third acceptor. However, the luminescence associated with the third acceptor is rather weak (see e.g. Ref. [92]) and could thus still be due to the In or Ga vacancy. The shallow donor could be the Cu interstitial or the In_{Cu} antisite. The Ga_{Cu} antisite in $CuGaSe_2$ is proposed to be deep – see below. Our proposal for the energies of defects in the band gap, based on these experimental and theoretical results is given in Figure 2.

Deep defects play an important role for Shockley-Read-Hall recombination. One way to measure the influence of recombination is the determination of photocarrier lifetimes by time resolved photoluminescence measurements. Only recently it was pointed out that the decay time of the photoluminescence signal gives information on the photocarrier lifetime only in special cases. In particular the measured decay time can be much longer than the lifetime due to trapping and detrapping effects [93]. The influence of detrapping effects can be detected by the temperature dependence of the decay behaviour [94]. The temperature dependence of the detrapping effect can be developed into a method to characterise the trap states themselves [95]. Besides affecting the doping density and the recombination behaviour, the electronic band structure is influenced by the details of the atomic structure: while the average bond lengths in $Cu(In,Ga)Se_2$ follow a linear Vegard's law, it was found by X-ray absorption measurements, that the In-Se and Ga-Se bond lengths remain essentially constant throughout the whole composition range between $CuInSe_2$ and $CuGaSe_2$ [96]. This leads to a non-linear displacement of the anions, which contributes to the bowing behaviour of the band gap. In a combined optical and theoretical study it was shown that the stability of the band gap with varying Cu-content can be due to an interplay between anion displacement and Cu vacancies [79].

Besides point defects extended defects play an important role in the absorber. A recent review can be found in Ref. [97].

Summary

Considerable progress has been made on the technological side by improving efficiencies and reducing raw material. This was combined with progress in the fundamental understanding of the material. Both trends have fruitfully interacted and entailed each other.

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* of special interest
** of outstanding interest

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